PATENT SPECIFICATION

NO DRAWINGS

1,003,083

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Int. Cl.:—C 07 d // C 08 f, g, D 06 l

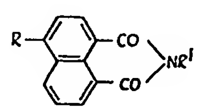
COMPLETE SPECIFICATION

Novel 4-Alkoxynaphthalimides

I, TOSHIYASU KASAI, a Japanese subject, of 3070, Midorigaoka, Meguro-ku, Tokyo, Japan, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

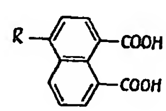
This invention relates to novel naphthalimide compounds which, when applied to off-white materials, absorb ultra-violet light from sunlight or fluorescent light and emit the absorbed energy as blue light, to processes for producing said compounds, and to a method of improving the brightness of polymeric materials by treatment with said compounds.

According to one aspect of the present invention there is provided a series of naphthalimide compounds which can be represented by the general formula:—



wherein R is a lower alkoxy group containing from 1 to 5 carbon atoms, preferably a methoxy or ethoxy group, and R¹ is a hydrogen atom or an alkyl, hydroxyalkyl, aminoalkyl, aralkyl, cycloalkyl, aryl, alkaryl or heterocyclic group, the aryl group being optionally substituted by a halogen atom or a hydroxyalkyl, alkylamino, alkoxy or —SO_3M group in which M is a hydrogen atom or an alkali metal atom. The radical R¹ may be, for example, hydrogen, methyl, ethyl, propyl, butyl, pentyl, hydroxymethyl hydroxyethyl, hydroxypropyl, N,N - dimethylaminopropyl, benzyl, cyclohexyl, phenyl, naphthyl, chlorophenyl, tolyl, 3¹ - methylolphenyl, 4¹ - methoxyphenyl, 4¹ - N,N - dimethylaminophenyl, sulphophenyl, 2,6 - dihalo - s - triazinyl, pyridyl or pyrazolyl.

The compounds of the present invention may be prepared by several methods. In one method a 4 - alkoxynaphthalic acid of the general formula:

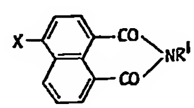


II

wherein R is defined as above, and/or the anhydride of said acid, is condensed

with ammonia or a primary amine having the general formula R^1NH_2 wherein R^1 is defined as above. 4 - Alkoxynaphthalic acids and acid anhydrides which may be used in the foregoing method include 4 - methoxynaphthalic acid, 4 - ethoxynaphthalic acid, 4 - propoxynaphthalic acid, 4 - butoxynaphthalic acid, 4 - methoxynaphthalic acid anhydride, 4 - ethoxynaphthalic acid anhydride, 4 - propoxynaphthalic acid anhydride and 4 - butoxynaphthalic acid anhydride. The ammonia may be used in the form of an aqueous ammoniacal solution or as liquid ammonia, and the primary amines which may be used include alkylamines, such as methylamine, ethylamine, isopropylamine, *n* - propylamine and butylamine, alkanolamines, such as methanolamine and ethanolamine, N,N - dialkylaminoalkylamines, such as N,N - dimethylaminoethylamine, cycloalkylamines, such as cyclopentylamine and cyclohexylamine, aralkylamines, such as benzylamine and *m*-, *o*-, and *p*-alkylbenzylamines, arylamines, such as aniline and naphthylamine, substituted arylamines such as halophenylamines, tolylamines, sulphonylamines, N,N - dialkylaminophenylamines, N,N - dialkylaminonaphthylamines, and heterocyclic amines, such as aminopyridine and aminopyrazole. Preferably the ammonia or primary amine is used in an amount which is stoichiometrically equimolar to, or in excess of, the amount of the naphthalic acid and/or the anhydride employed. The reaction may be carried out in water or in an organic solvent, e.g. glacial acetic acid, lower aliphatic alcohols and benzene. The reaction is generally carried out at a temperature above 70°C. and is preferably carried out at a temperature of from 100 to 110°C. A condensation catalyst can be used if desired, although the use of such a catalyst is not critical. The 4 - alkoxynaphthalic acid or acid anhydride starting materials can be prepared by reacting 5 - hydroxyacenaphthene with an alkylating agent, e.g. a dialkyl sulphate, such as dimethyl sulphate or diethyl sulphate, or an alkyl halide, e.g. methyl bromide, ethyl bromide, methyl iodide or ethyl iodide, to form a 5 - alkoxyacenaphthene which can then be treated with an oxidizing agent, such as an alkali metal bichromate or an alkali metal permanganate, to form the desired 4 - alkoxynaphthalic acid or its anhydride.

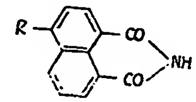
The compounds of the present invention can also be prepared by replacing the radical X of a compound of the general formula:



, III

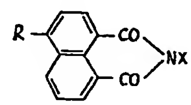
wherein X is a halogen atom, a hydroxy group, a nitro group, an amino group, a diazonium group or a sulphonic acid group, and R^1 is defined as above by a lower alkoxy group R. This may be achieved by reacting a compound of general formula III above when X is a halogen atom, a hydroxy group, a nitro group or a sulphonic acid group with, for example, an alkali metal alcoholate, e.g. sodium methylate or sodium ethylate, or with a combination of an alkali metal and a lower aliphatic alcohol, e.g. sodium and methanol or ethanol. Alternatively, when X is a hydroxyl group it can be replaced by the radical R by reacting a compound of general formula III with a dialkyl sulphate or an alkyl halide. In general, the reaction can be carried out by mixing the reactants together in approximately stoichiometric proportions and heating the resulting mixture, with stirring, to a temperature in the region of the boiling point of the mixture under atmospheric or superatmospheric pressure up to about 10 atmospheres. If desired, a catalyst, such as is commonly known to those skilled in the art, can be added to the reaction mixture, the catalyst may be, for example, potassium acetate or copper acetate. The reaction may be carried out with or without a solvent, e.g. water or an organic solvent such as an alcohol, e.g. methanol or ethanol, or benzene. When X of formula III above is an amino group, the desired compound can be obtained by converting the amino group to a diazonium group and thereafter reacting the diazonium compound with a lower aliphatic alcohol containing from 1 to 5 carbon atoms. Compounds of general formula III which may be employed in this method include, for example, 4 - chloronaphthalimide (m.p. 301—302°C.) and its N - substituted derivatives, 4 - bromonaphthalimide (m.p. 286°C.) and its N - substituted derivatives, 4 - hydroxynaphthalimide (m.p.>350°C.) and its N - substituted derivatives, 4 - nitrophthalimide (m.p. 287—8°C.) and its N - substituted derivatives, 4 - aminonaphthalimide and its N - substituted derivatives, 4 - sulphonanaphthalimide and its N - substituted derivatives and 4 - diazoniumnaphthalimide and its N - substituted derivatives.

The compounds of the present invention wherein R^1 of general formula I is not hydrogen can also be prepared by reacting a compound of the general formula:—



I^1

i.e. a compound of general formula I in which R^1 is hydrogen, or an alkali metal salt thereof with a compound of the general formula $R^{11}X$ wherein R^{11} is an alkyl, hydroxyalkyl, aminoalkyl, aralkyl, cycloalkyl, aryl, alkaryl or heterocyclic group, the aryl group being optionally substituted by a halogen atom or a hydroxyalkyl, aminoalkyl, alkoxy or SO_3M group in which M is a hydrogen atom or an alkali metal atom, and X is a halogen atom. In a still further method the compounds of the present invention can be prepared by reacting a compound of the general formula:—



I^{11}

(which compound can be prepared by dissolving the corresponding compound of general formula I^1 in an alkaline solution and then salting out the compound of general formula I^{11} from the solution by the addition thereto of an alkali metal halide) with a compound of the general formula $R^{11}OH$ wherein R^{11} is defined as above. Suitable reaction media, catalysts and other reaction conditions for effecting these condensation reactions can be selected by those skilled in the art with reference to the properties of the desired novel compounds. The reaction whereby a compound of general formula I^{11} is converted to a compound of general formula I is of particular value where R^{11} is the 2,6 - dihalo - s - triazinyl radical. More particularly, a 4 - alkoxynaphthalimide, or an alkali metal salt thereof, can be condensed with cyanuric halide at the approximate molar ratio of 1:1 to produce the corresponding 4 - alkoxynaphthal - N - (2,4 - dihalo - s - triazinyl) - imide. The imides are particularly suitable for whitening natural fibres, e.g. woollen fibres.

The novel compounds of the present invention are normally pale yellow or creamy white crystalline materials, which can yield colourless, clear solutions in water or organic solvents. They are only moderately soluble in water but are soluble in methanol, ethanol, and acetic acid. Generally, they are stable to light, heat and other forms of physical or chemical attack. The compounds when dispersed or dissolved in water or an alcohol are substantive to high molecular weight natural and synthetic polymers. Articles which are made from said polymers and which have been treated with the compounds of the present invention exhibit good light fastness, laundry fastness and have imparted thereto and improved brightness. Accordingly, the compounds of the present invention can be used as optical brightening agents for high molecular weight polymers and articles formed therefrom. Such articles may be in a form of filaments, yarns, threads, films, sheets, ribbons, foils or plates or in fact in any shape or form. The compounds of the invention are particularly suitable for use in the optical brightening of textile materials made of natural or man-made fibres or filaments. Thus, they may be used in the optical brightening of vegetable fibrous materials e.g. cotton, capoc, linen, sisal and jute, animal fibrous materials e.g. wool, mohair and cashmere, mineral fibrous materials e.g. asbestos, natural polymer man-made fibrous materials e.g. regenerated cellulose, such as viscose rayon, and cellulose acetate, and synthetic polymer man-made fibrous materials comprising organic materials, e.g. polyamides, polyesters, polyurethanes, polyvinyl chloride, polyvinylidene chloride, polyacrylonitrile and polyvinyl alcohol, or inorganic materials, e.g. glass fibre. The compounds of the present invention can be permeated into or dyed on the high molecular weight polymers after they have been fabricated to a desired form or shape; alternatively, they can be incorporated in or combined with the high molecular weight polymers before they have been fabricated to a particular shape or form. Thus, for example, one or more of the compounds of the invention may be incorporated in a mass comprising a filament- or film-forming high molecular weight

polymeric material in an amount of from 0.1 to 2.0% based on the weight of the high polymeric material, and then the mass formed into the desired filament or film by spinning or extrusion.

The use of the compounds of the present invention an optical brightening agent for textile materials may be illustrated by reference to the treatment of polyester fibres. In the treatment of polyester fibres one or more imide compounds of the invention is or are uniformly dispersed or dissolved in water or a suitable solvent, with or without a suitable dispersing agent, e.g. a surface active agent. Polyester fibre is treated with the resulting dispersion or solution in a conventional manner, e.g. by ordinary dyeing, carrier dyeing, high temperature dyeing or thermosol dyeing. The polyester fibres so treated absorb ultraviolet light from sunlight or a fluorescent light source and emit the absorbed energy as blue light. Thus, textile materials which are not coloured have imparted thereto a permanently durable white appearance through compensation for yellow tints, and those textile materials which are coloured have imparted thereto an improved purity of the original colour and with added brightness.

The invention is further illustrated by the following Examples.

EXAMPLE 1

Ten grams of 4 - methoxynaphthalic anhydride were reacted with 100 ml. of 28% aqueous solution of ammonia for one hour under reflux. After completion of the reaction, the resulting reaction mixture was cooled and then filtered. 9.5 g. of 4 - methoxynaphthalimide having a m.p. of 320—2°C. were obtained, the yield being 97% on the theoretical. After recrystallization from glacial acetic acid, pure 4 - methoxynaphthalimide in the form of pale yellow crystals and melting at 320—1°C. was obtained. The result of elementary analysis was as follows:

Calcd.	N : 5.90%
Found.	N : 6.09%

EXAMPLE 2

Ten grams of 4 - methoxynaphthalic anhydride were reacted with 100 ml. of an aqueous solution of 10% methylamine for one hour under reflux. After completion of the reaction, the resulting reaction mixture was cooled and filtered, whereby 9.7 g. of 4 - methoxynaphthalmethylimide melting at 197—201°C. were recovered as a pale yellow powder, the yield being 91% on the theoretical. After recrystallization of this powder from glacial acetic acid, pure crystalline 4 - methoxynaphthalmethylimide melting at 200°—201°C. was obtained. The result of elementary analysis was as follows:

Calcd.	N : 5.80%
Found.	N : 5.95%

EXAMPLE 3

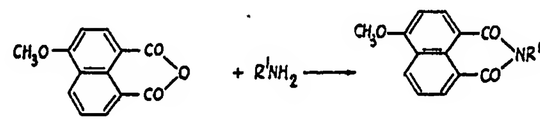
Ten grams of 4 - methoxynaphthalic anhydride were reacted with 100 ml. of an aqueous solution of 10% ethylamine for one hour under reflux. After completion of the reaction, the resulting reaction mixture was cooled and filtered. 10.5 g. of 4 - methoxynaphthalethylimide were obtained as a pale yellow powder in a yield of 94% on the theoretical. On recrystallization of the powder from glacial acetic acid, pure pale yellow crystalline 4 - methoxynaphthalethylimide melting at 152—3°C. was obtained. The result of elementary analysis was as follows:

Calcd.	N : 5.49%
Found.	N : 5.57%

EXAMPLES 4—12

The procedure described in Example 3 was repeated using the reagents given in Table I below whereby a number of 4 - methoxynaphthal - N - substituted - imides were obtained.

TABLE I



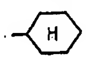
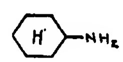
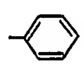
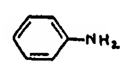
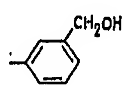
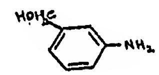
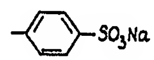
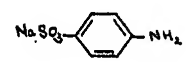
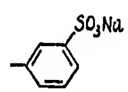
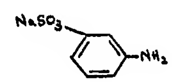
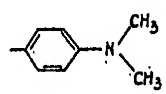
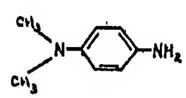
Ex.	R^1	Type of amines	Crude imides		Pure imides	
			m.p.	Yield	m.p.	Elementary analysis
4	n—C_3H_7	n—$C_3H_7NH_2$	93—6°C.	88.0%	111.5—2.5°C.	Nc:5.20% Nf:5.36%
5	i—C_3H_7	i—$C_3H_7NH_2$	197—9°C.	29.0%	198—9°C.	Nc:5.20% Nf:5.26%
6	n—C_4H_9	n—$C_4H_9NH_2$	100—3°C.	78.0%	115—6°C.	Nc:4.93% Nf:5.12%
7			173—6°C.	100.0%	186.5—7.5°C.	Nc:4.53% Nf:4.55%
8			206—7°C.	100.0%	235—6°C.	Nc:4.62% Nf:4.40%

TABLE I—*continued*

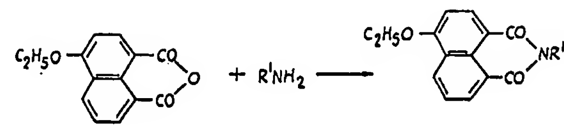
Ex.	R^1	Type of amines	Crude imides		Pure imides	
			m.p.	Yield	m.p.	Elementary analysis
9			223—6°C.	95.5%	227.5—9°C.	Nc:4.20% Nf:4.24%
10			—			
11			—			
12			317—8°C.	67.5%		

(Note) Nc is the calculated percentage nitrogen content of the imide and Nf is the percentage nitrogen content found experimentally.

EXAMPLES 13—23

4 - Ethoxynaphthalic acid anhydride (m.p. 183—4°C) was condensed with a variety of amine reagents as given in Table II below (including ammoniacal water) in the manner described in the preceding Examples to give a number of 4 - ethoxy-naphthal - N - substituted - imides.

TABLE II



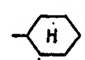
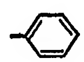
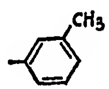
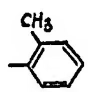
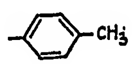
Ex.	R^1	m.p.	Yield	Elementary analysis	Appearance
13	—H	261.5—262°C.	90.3%	Nc:5.80% Nf:5.65%	Pale yellow crystalline needles
14	$—CH_3$	173.5—4°C.	—		Pale yellow crystalline needles
15	$—C_2H_5$	132.5—133°C.	94.5%	Nc:5.20% Nf:5.07%	Pale yellow crystalline needles
16	—*n*—C_3H_7	132.5—133°C.	96.0%	Nc:4.94% Nf:4.89%	Pale yellow crystalline needles
17	—isoC_3H_7	135—135.5°C.	31.4%	Nc:4.94% Nf:4.81%	Pale yellow crystalline needles
18	—nC_4H_9	133—4°C.	97.0%	Nc:4.71% Nf:5.03%	Pale yellow crystalline needles
19		195.5—196°C.	40.3%	Nc:4.23% Nf:4.15%	Pale yellow crystalline needles

TABLE II—continued

Ex.	R¹	m.p.	Yield	Elementary analysis	Appearance
20		243—247°C.	—		Brown crystalline needles
21		187.5—188.5°C.	—		Yellow crystalline needles
22		195.5—196.5°C.	—		—
23		266—267°C.	—		Dry white crystalline plates

EXAMPLE 24

6.36 g. of 4 - nitronaphthalphenylimide were dissolved in 2000 ml. of methanol. To the resulting solution there were added 10.8 g. of sodium methylate and a catalytic amount of copper acetate. The resulting mixture was refluxed for 5 hours. After completion of the reaction, the reaction mixture was distilled to remove methanol therefrom after which it was admixed with water and glacial acetic acid and then filtered. 5.50 g. of 4 - methoxynaphthalphenylimide were recovered as a pale yellow precipitate. On repeated recrystallization, pure crystalline 4 - methoxynaphthalphenylimide was obtained as pale yellow crystalline needles.

EXAMPLE 25

The procedure described in Example 24 was repeated using 4 - nitronaphthal alkyl, cycloalkyl or arylimides listed below instead of the 4 - nitronaphthalphenylimide used in Example 24 to produce the corresponding 4 - methoxynaphthal - N - substituted imides.

4 - Nitronaphthalmethylimide (m.p. 208—9°C.),
4 - Nitronaphthalethylimide (m.p. 187.5—188.5°C.),
4 - Nitronaphthal - *n* - propylimide (m.p. 135.5—136.5°C.),
4 - Nitronaphthalisopropylimide (m.p. 253.5—255°C.),
4 - Nitronaphthal - *n* - butylimide (m.p. 103.5—104.5°C.),
4 - Nitronaphthalisopentylimide (m.p. 134—5°C.),
4 - Nitronaphthalhydroxyethylimide (m.p. 155.5—156.5°C.),
4 - Nitronaphthalcyclohexylimide (m.p. 209.5—210.5°C.),
4 - Nitronaphthal - *o* - methylphenylimide (m.p. 230—1°C.),
4 - Nitronaphthal - *p* - methylphenylimide (m.p. 246—7°C.),
4 - Nitronaphthal - *o* - chlorophenylimide (m.p. 207—8°C.),
4 - Nitronaphthal - *p* - chlorophenylimide (m.p. 274—5°C.),
and 4 - Nitronaphthal - *p* - methoxyphenylimide (m.p. 249—251°C.).

EXAMPLE 26

10.2 g. of 4 - Chloronaphthalphenylimide (m.p. 241—3°C.) were dissolved in 2000 ml. of methanol. To the resulting solution there were added 18 g. of sodium methylate and a catalytic amount of copper acetate. The resulting mixture was refluxed for 5 hours. After completion of the reaction, the reaction mixture was distilled to remove methanol therefrom, after which it was admixed with water plus glacial acetic acid and then filtered. 8.50 g. of 4 - methoxynaphthalphenylimide were obtained as a pale yellow precipitate. On repeated recrystallization from glacial acetic acid, pure crystalline 4 - methoxynaphthalphenylimide was obtained as pale yellow crystalline needles. The result of elementary analysis was as follows:

Calcd.	N : 4.62%
Found.	N : 4.50%

EXAMPLE 27

The procedure described in Example 26 was repeated using the 4 - halonaphthalimide compounds listed below instead of the 4 - chloronaphthalphenylimide used in Example 26 to produce the corresponding 4 - methoxynaphthal - N - substituted or unsubstituted imides.

4 - Chloronaphthalmethylimide (m.p. 174—5°C.)
4 - Chloronaphthalbutylimide (m.p. 92—4°C.)
4 - Chloronaphthal - *p* - tolylimide (m.p. 240—2°C.)
4 - Chloronaphthal - *p* - anisylimide (m.p. 227—8°C.)
4 - Bromonaphthalbutylimide (m.p. 104—5°C.)
4 - Chloronaphthalimide (m.p. 301—2°C.)
4 - Bromonaphthalimide (m.p. 286°C.)

EXAMPLE 28

4 - Aminonaphthalmethylimide was dissolved in an dilute aqueous hydrochloric acid solution and to the resulting solution there was added an aqueous sodium nitrite solution. Upon addition of ether to the resulted reaction mixture, the diazonium salt of 4 - aminonaphthalmethylimide separated out. This compound was collected by filtration and then dissolved in 75% methanol. After stirring of the solution at 50—60°C. for one hour, the desired crystalline 4 - methoxynaphthalmethylimide

appeared and was collected by filtration and then washed with dilute methanol, m.p. 344—6°C.

Each of the following 4 - aminonaphthalimides and N - substituted imides was converted into the corresponding 4 - alkoxynaphthalimide or N - substituted imide by the general procedure described above.

4 - Aminonaphthalimide (m.p.>360°C.)
4 - Aminonaphthalethylimide (m.p. 279—280°C.)
4 - Aminonaphthal - *n* - propylimide (m.p. 249—250.5°C.)
4 - Aminonaphthalisopropylimide (m.p. 350°C.)
4 - Aminonaphthal - *n* - butylimide (m.p. 185—186°C.)
4 - Aminonaphthalisopentylimide (m.p. 166.5—167.5°C.)
4 - Aminonaphthalhydroxyethylimide (m.p. 260—1°C.)
4 - Aminonaphthalcyclohexylimide (m.p. 242—3°C.)
4 - Aminonaphthalphenylimide (m.p. 302—4°C.)
4 - Aminonaphthal - *o* - methylphenylimide (m.p. 300—2°C.)
4 - Aminonaphthal - *p* - methylphenylimide (m.p. 343—5°C.)
4 - Aminonaphthal - *o* - chlorophenylimide (m.p. 299—302°C.)
4 - Aminonaphthal - *p* - chlorophenylimide (m.p.>360°C.)
4 - Aminonaphthal - *p* - methoxyphenylimide (m.p. 358—360°C.)
4 - Aminonaphthal - *m,o* or *p* - xylylimides

EXAMPLE 29

Two gram samples of polyethylene terephthalate fibre were dipped at 100°C. for one hour into aqueous dispersions containing 2% 4 - methoxynaphthalimide (m.p. 320—1°C.), 4 - methoxynaphthalmethylimide (m.p. 200—1°C.) and 4 - methoxynaphthalethylimide (m.p. 152—3°C.), respectively. In all cases, the polyester fibre had an improved white appearance after treatment.

EXAMPLE 30

Polyethylene terephthalate fibre was dipped at 60°C. into a dyeing bath having the following formulation:

4 - Methoxynaphthalimide	0.5—3%
Anionic or nonionic surfactant	0.5 g./l.
Bath ratio	1 : 20 — 1 : 50

The bath temperature was raised up to 98—100°C. and, at this temperature, dyeing was effected for 60 minutes. The dyed fibre was washed with water.

EXAMPLE 31

Polyethylene terephthalate fibre was dyed with the same dyeing bath as was used in Example 30 at 120°C. for 30—45 minutes by means of a high temperature dyeing machine, and then it was washed with water. In this case the dyeing was effected in a shorter time than that required when using a commonly known whitening agent for polyester fibres.

EXAMPLE 32

A solution was prepared having the following formulation:

4 - Methoxynaphthalimide	5 — 20 g./l.
Carboxymethyl cellulose	1 g./l.
Water	1 l.

Polyethylene terephthalate fabric was padded in this solution at 30—50°C., squeezed to a moisture content of 50—70%, subjected to moderate drying at 80—90°C. for 2 minutes by means of a hot air dryer and then heated at 180°—200°C. for 15 seconds. Then the padded fabric was soaped in a bath containing a neutral synthetic detergent (2 g./l.) at a bath ratio of 1 : 20 to 1 : 50 at 60°—70°C. for 10 minutes and thereafter washed with water.

EXAMPLE 33

Polyethylene terephthalate fibre was dipped at about 60°C. in a bath containing:

4 - Ethoxynaphthalimide	0.5 — 3%
Anionic or nonionic surfactant	0.5 g./l.
Chlorobenzene-type carrier	10 — 15%
Bath ratio	1 : 20 — 1 : 50

The bath temperature was raised to 98°—100°C. over a period of about 20 minutes. At this temperature, dyeing was effected for 30 minutes. The fibre so treated was soaped in a bath containing a neutral synthetic detergent (2 g./L.) at a bath ratio of 1 : 20—1 : 50 at 60°—70°C. for 10 minutes and thereafter washed with water.

EXAMPLE 34

An aqueous bleaching bath having the following formulation was prepared:

4 - Methoxynaphthalimide	0.5 — 3%
Sodium hypochlorite	5—10%
Chlorous dioxide gas generation inhibitor	2.5 — 5%
Bath temperature	1 : 20 — 1 : 50

The bath was adjusted to a pH of 3—4 by the addition of 2—5% glacial acetic acid. Dyeing was started at a bath temperature of about 60°C. and then the temperature was raised to 98° — 100°C. over a period of about 20 minutes. Polyacrylonitrile fibre was maintained at that temperature for 30° — 60 minutes and then gradually cooled down to 70°C. The treated fibre was washed with water, treated with a sodium bisulphite (1 g./L.) solution at 60—70°C. for one hour and then washed with water. In this way whitening (optical brightening) and chemical bleaching were effected simultaneously.

The optical brightening properties of the organic compounds of this invention are illustrated by the following data:

Light fastness expressed by change in relative intensiveness of fluorescence

Type of fibres treater	Irradiation time (hr)				
	0	50	10	20	30
Polyethylene terephthalate	100	100	99	97	95
Polyacrylonitrile	100	98	95	93	90
Cellulose acetate	100	100	99	97	95

In each of the runs, a solution of 2% 4 - methoxynaphthalimide was used to treat the fibres. The polyethylene terephthalate fibre was treated by high temperature dyeing, the polyacrylonitrile fibre was treated with a bath containing 2% 4 - methoxynaphthalimide in combination with sodium hypochlorite, and the cellulose acetate was treated by a conventional dip dyeing process.

Laundry fastness expressed by change in relative intensiveness of flourescence

Method of testing	Type of fibre treated		
	Polyethylene terephthalate	Polyacrylo-nitrile	Cellulose acetate
Before testing	100	100	100
MC—2	102	102	97
MC—3	102	101	93

The samples used were the same as those used in the preceding test for light fastness. The procedures MC — 2 and MC — 3 are described in JIS—L—1045 (1959).

Perspiration fastness expressed by change in relative intensiveness of fluorescence

Method of testing	Type of fibre treated		
	Polyethylene terephthalate	Polyacrylonitrile	Cellulose acetate
Before testing	100	100	100
B—method (Acidic conditions)	101	102	104
B—method (Alkaline conditions)	103	100	103

The procedure for B-method are described in JIS—L—1047 (1959).

EXAMPLE 35

21.1 g. of sodium hydroxide and 50.0 g. of 4 - hydroxynaphthalmethylimide were dissolved in 500 ml. of water. To the resulting solution there were added gradually 55.5 g. of dimethyl sulphate. Reaction was effected at 30°C. for 1 hour and then at 60°C. for another hour, while stirring. After completion of the reaction, the reaction mixture was filtered, whereby unreacted materials were passed to the filtrate. The precipitate recovered was washed with a dilute aqueous solution of sodium carbonate and then with water and thereafter it was dried. After recrystallization from acetic acid, 4 - methoxynaphthalmethylimide melting at 198.8—199.2°C. was obtained in a yield of 15 g.

EXAMPLE 36

33.6 g. of sodium carbonate and 30.0 g. of 4 - hydroxynaphthalmethylimide were dissolved in 300 ml. of water. To the resulting solution there were added gradually 81.4 g. of diethyl sulphate. Reaction was effected at 60°C. for 2 hours and then at 95°C. for 15 minutes. After completion of the reaction, the resulting product was worked up in the same manner as described in Example 35 to yield 15.0 g. of 4 - ethoxynaphthalmethylimide melting at 167.5—168.3°C.

EXAMPLE 37

56.2 g. of ethyl iodide were added slowly to a mixture of 300 ml. of water, 16.1 g. of sodium carbonate and 30.0 g. of 4 - hydroxynaphthalmethylimide. The resulting total mixture was heated under reflux for 3 hours. After completion of the reaction, the resulting product was worked up in the manner described in Example 36 to yield 4.0 g. of 4 - ethoxynaphthalmethylimide.

EXAMPLE 38

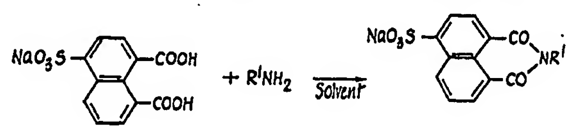
The procedures described in Example 36 and 37 were repeated using the following 4 - hydroxynaphthal - alkyl, -cycloalkyl, -aralkyl and -aryl imides to produce the corresponding 4 - ethoxynaphthal - N - substituted imides.

4 - Hydroxynaphthalmethylimide (m.p. 303.5—305.5°C.)
4 - Hydroxynaphthalbutylimide (m.p. 165.5—166.5°C.)
4 - Hydroxynaphthalhydroxyethylimide (m.p. 195.5—196.2°C.)
4 - Hydroxynaphthalaminoethylimide (m.p. 162.5°C. (decomp))
4 - Hydroxynaphthalcyclohexylimide (m.p. 286.5—288.0°C.)
4 - Hydroxynaphthalbenzylimide (m.p. 190.0—191.5°C.)
4 - Hydroxynaphthalphenylimide (m.p. 330°C.)

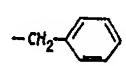
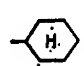
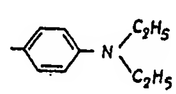
Example 39

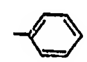
(A) Naphthalimide - 4 - sulphonates and the N - substituted derivatives thereof, all which can be converted into 4 - alkoxynaphthalimide or the N - substituted derivatives thereof, were prepared in accordance with the following procedure:

20.0 g. of sodium naphthalic acid - 4 - sulphonate were added to 40 g. of an aqueous solution containing 10% methylamine. Reaction was effected at 15—30°C. for 5 hours. After completion of the reaction, the reaction mixture was filtered. The precipitate obtained was washed with saline water and then dried, thus producing white crystalline sodium naphthalmethylimide - 4 - sulphonate in a yield of 18.3 g.



In a similar manner, the compounds set forth below were prepared.

R^1	Amount of R^1NH_2	Amount of sodium naphthalic acid-4-sulphonate	Solvent	Yield of Sodium naphthalimide-4-sulphonate compounds.
n—C_4H_9	73.0 g.	63 g.	100 g. H_2O	67.4 g.
—CH_2CH_2OH	9.6 g.	10 g.	86.5 g. H_2O	11.2 g.
	16.8 g.	10 g.	151 g. H_2O	11.0 g.
	6.2 g.	10 g.	56 g. H_2O	10.2 g.
	82.6 g.	82.6 g.	750 g. H_2O	93.5 g.

R[1]	Amount of R^1NH_2	Amount of sodium naphthalic acid-4-sulphonate	Solvent	Yield of Sodium naphthalimide-4-sulphonate compounds.
	50.0 g.	50.0 g.	250 ml. MeOH plus 200 ml. H_2O	38.6 g.
$-CH_2-CH(-(CH_2)_3-CH_3)-C_2H_5$	78 g.	64.0 g.	350 ml. EtOH plus 350 ml. H_2O	44 g.
$-(CH_2)_3-N(CH_3)_2$	14.0 g.	14.5	120 ml. H_2O	10.5 g.

(Note) Melting points of the products were unmeasurable because all were in the form of alkali metal sulphonate.

(B) Sodium naphthal alkyl or aryl imide - 4 - sulphonates prepared as described above were converted to the corresponding 4 - alkoxynaphthal alkyl or aryl imides by the following procedure:

30 g. of sodium naphthalmethylimide - 4 - sulponate were added to a solution of 30 g. NaOH in 300 g. methanol. The resulting mixture was refluxed, with stirring, for 10 hours. After completion of the reaction, the resulting reaction mixture was cooled and then filtered. The separated precipitate was washed with methanol and then with warm water and dried. 22.8 g. of 4 - methoxynaphthalmethylimide having a melting point of 198.8—199.2°C. were obtained. The analysis for $C_{14}H_{11}NO_3$ was:

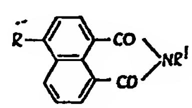
Calcd.	C 69.70%, H 4.59%, N 5.80%
Found.	C 69.61%, H 4.84%, N 5.73%

In the same way as described above, the reactants A and B set forth in the following Table were reacted together to form the corresponding product C:

A	B	C
Ethanol	Sodium naphthal-methylimide-4-sulphonate	4-Ethoxynaphthal-methylimide
n-Butanol	Sodium naphthal-methylimide-4-sulphonate	4-n-Butoxynaphthalmethylimide
Methanol	Sodium naphthal-butylimide-4-sulphonate	4-Methoxynaphthal-butylimide
Methanol	Sodium naphthal-2^1-hydroxyethyl-imide-4-sulphonate	4-Methoxynaphthal-2^1-hydroxyethyl-imide
Methanol	Sodium naphthal-benzylimide-4-sulphonate	4-Methoxynaphthal-benzylimide
Methanol	Sodium naphthal-cyclohexylimide-4-sulphonate	4-Methoxynaphthal-cyclohexylimide
Methanol	Sodium naphthal-N^1-N^1-dimethylamino-propylimide-4-sulphonate	4-Methoxynaphthal-N^1,N^1-dimethyl-aminopropylimide

WHAT WE CLAIM IS:—

1. A naphthalimide compound which can be represented by the general structural formula:



wherein R is a lower alkoxy group containing from 1 to 5 carbon atoms, and R^1 is a hydrogen atom or an alkyl, hydroxyalkyl, aminoalkyl, aralkyl, cycloalkyl, aryl, alkaryl or a heterocyclic group, the aryl group being optionally substituted by a halogen atom or a hydroxyalkyl, alkylamino, alkoxy or $-SO_3M$ group in which M is a hydrogen atom or an alkali metal atom.

2. A compound according to Claim 1, wherein R is a methoxy or ethoxy group.

3. 4 - Methoxynaphthalimide.

4. 4 - Methoxynaphthalmethylimide.

5. 4 - Methoxynaphthalethylimide.

6. 4 - Methoxynaphthal - *n* - propylimide.

7. 4 - Methoxynaphthalisopropylimide.

8. 4 - Methoxynaphthal - *n* - butylimide.

9. 4 - Methoxynaphthalcyclohexylimide.

10. 4 - Methoxynaphthalphenylimide.

11. 4 - Methoxynaphthal - *m* - hydroxymethylphenylimide.

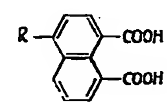
12. 4 - Methoxynaphthal - *p* - N,N - dimethylaminophenylimide.

13. 4 - Methoxynaphthalsulphophenylimides and the alkali metal salts thereof.

14. 4 - Ethoxynaphthalimide.

15. 4 - Ethoxynaphthalmethylimide.
16. 4 - Ethoxynaphthalethylimide.
17. 4 - Ethoxynaphthal - *n* - propylimide.
18. 4 - Ethoxynaphthalisopropylimide.
19. 4 - Ethoxynaphthal - *n* - butylimide.
20. 4 - Ethoxynaphthal - cyclohexylimide.
21. 4 - Ethoxynaphthal - phenylimide.
22. 4 - Ethoxynaphthal - *o* - tolylimide.
23. 4 - Ethoxynaphthal - *m* - tolylimide.
24. 4 - Ethoxynaphthal - *p* - tolylimide.

25. A method of preparing a compound as claimed in Claim 1, which comprises condensing a compound which can be represented by the general structural formula:

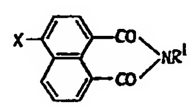


with ammonia or a primary amine having the general formula R^1NH_2 wherein R^1 is defined as in Claim 1.

26. A method according to Claim 25, wherein the condensation reaction is carried out at a temperature of from 100° to 110°C.

27. A method according to Claim 25 or 26, wherein the condensation reaction is carried out in the presence of a condensation catalyst.

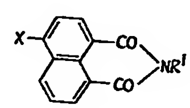
28. A method of preparing a compound as claimed in Claim 1, which comprises reacting a compound which can be represented by the general structural formula:



wherein R^1 is defined as in Claim 1 and X is a halogen atom, a hydroxy group, a nitro group or a sulphonic acid group, with an alkali metal alcoholate containing from 1 to 5 carbon atoms or with a mixture of a lower alcohol containing from 1 to 5 carbon atoms and an alkali metal.

29. A method according to Claim 28, wherein the reaction is carried out at a temperature in the region of the boiling point of the mixture of reactants at a pressure in the range of from 1 to 10 atmospheres.

30. A method of preparing a compound as claimed in Claim 1, which comprises converting a compound which can be represented by the general structural formula:



wherein X is an amino group, to the corresponding diazonium compound and thereafter reacting the diazonium compound with a lower aliphatic alcohol containing from 1 to 5 carbon atoms.

31. A method according to Claim 28 or 29, wherein the reaction is carried out in the presence of a catalyst known for such reactions.

32. A method according to Claim 28, 29 or 31, wherein the reaction is carried out in water, methanol; ethanol or benzene.

33. A method of preparing a compound as claimed in Claim 1, substantially as described in any one of the foregoing Examples 1 to 28, and 35 to 39.

34. A process for optically brightening an article made from a natural or synthetic high molecular weight polymer, which comprises treating said article with a compound claimed in any one of Claims 1 to 24.

35. A process according to Claim 34, wherein said article is a textile material.

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